

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date  
25 March 2004 (25.03.2004)

PCT

(10) International Publication Number  
WO 2004/025748 A1

(51) International Patent Classification<sup>7</sup>: H01L 51/20, (74) Common Representative: AGFA-GEVAERT; Corporate IP Department (3800), Septestraat 27, B-2640 Mortsel (BE).

(21) International Application Number:

PCT/EP2002/010120

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date:  
10 September 2002 (10.09.2002)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant (for all designated States except US): AGFA-GEVAERT [BE/BE]; Septestraat 27, B-2640 Mortsel (BE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): ANDRIESSEN, Hieronymus [NL/BE]; Agfa-Gevaert, Corporate IP Department (3800), Septestraat 27, B-2640 Mortsel (BE). VAN DEELEN, Joop [NL/NL]; Energieonderzoek Centrum Nederland, Postbus 1, NL-1755 ZG Petten (NL). WIENK, Martijn [NL/NL]; Technische Universiteit Eindhoven, Postbus 513, NL-5600 MB Eindhoven (NL). KROON, Jan [NL/NL]; Energieonderzoek Centrum Nederland, Postbus 1, NL-1755 ZG Petten (NL).

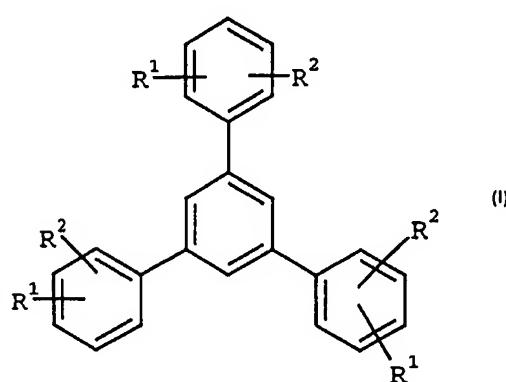
(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- with amended claims

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PHOTOVOLTAIC DEVICE COMPRISING A 1,3,5-TRIS-AMINOPHENYL-BENZENE COMPOUND



layer with a solution or dispersion comprising the 1,3,5-tris-aminophenyl-benzene compound, or cation thereof, to provide after drying a layer comprising the 1,3,5-tris-aminophenyl-benzene compound; and applying a conductive layer to the layer comprising the 1,3,5-tris-aminophenyl-benzene compound thereby providing a second electrode.

(57) Abstract: A photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV, a spectral sensitizer and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I): wherein R1 represents a -NR3R4 group, wherein R3 and R4, same or different, represents a C2-C10 alkyl group including the alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R2 represents hydrogen, an alkyl group including a substituted alkyl group or halogen; and the 1,3,5-tris-aminophenyl-benzene compound is optionally in a cationic form; and a process for preparing the above-mentioned photovoltaic device with at least one transparent electrode comprising the steps of: providing a support with a conductive layer as one electrode; coating the conductive layer on the support with a layer comprising the n-type semiconductor with a bandgap of greater than 2.9 eV; coating the n-type semiconductor-containing

## PHOTOVOLTAIC DEVICE COMPRISING A 1,3,5-TRIS-AMINOPHENYL-BENZENE COMPOUND

## Field of the invention

5

The present invention relates to a photovoltaic device comprising a 1,3,5-tris-aminophenyl-benzene compound optionally in a cationic form.

## 10 Background of the invention.

There are two basic types of photoelectrochemical photovoltaic cells. The first type is the regenerative cell which converts light to electrical power leaving no net chemical change behind. 15 Photons of energy exceeding that of the band gap generate electron-hole pairs, which are separated by the electrical field present in the space-charge layer. The negative charge carriers move through the bulk of the semiconductor to the current collector and the external circuit. The positive holes are driven to the surface 20 where they are scavenged by the reduced form of the redox relay molecular (R), oxidizing it:  $h^+ + R \rightarrow O$ , the oxidized form. O is reduced back to R by the electrons that re-enter the cell from the external circuit. In the second type, photosynthetic cells, operate on a similar principle except that there are two redox 25 systems: one reacting with the holes at the surface of the semiconductor electrode and the second reacting with the electrons entering the counter-electrode. In such cells water is typically oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. Titanium dioxide has been the favoured 30 semiconductor for these studies.

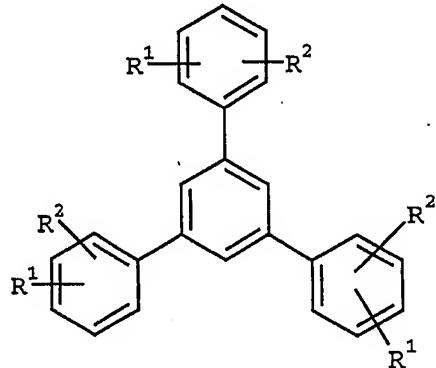
Mesoscopic or nano-porous semiconductor materials, minutely structured materials with an enormous internal surface area, have been developed for the first type of cell to improve the light capturing efficiency by increasing the area upon which the 35 spectrally sensitizing species could adsorb. Arrays of nano-crystals of oxides such as  $TiO_2$ ,  $ZnO$ ,  $SnO_2$  and  $Nb_2O_5$  or chalcogenides such as CdSe are the preferred semiconductor materials and are interconnected to allow electrical conduction to take place. These fundamental techniques were disclosed in 1991 by 40 Graetzel et al. in *Nature*, volume 353, pages 737-740 and in US 4,927,721, US 5,350,644 and JP-A 05-504023. Graetzel et al.

reported solid-state dye-sensitized mesoporous  $TiO_2$  solar cells with up to 33% photon to electron conversion efficiencies.

EP-A 1 176 646 discloses a solid state p-n heterojunction comprising an electron conductor and a hole conductor, characterized in that it further comprises a sensitizing semiconductor, said sensitizing semiconductor being located at an interface between said electron conductor and said hole conductor; and its application in a solid state sensitized photovoltaic cell.

There is therefore a requirement for thermally stable organic hole-conducting compounds capable of forming stable transparent layers and being compatible with solid state photovoltaic cell configurations.

EP 0 349 034 discloses a chemical compound corresponding to. the following general formula:



15 wherein  $R^1$  represents a  $-NR^3R^4$  group, wherein  $R^3$  and  $R^4$ , same or different, represents a  $C_2-C_{10}$  alkyl group including said alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and  $R^2$  represents hydrogen, an alkyl group including a substituted alkyl group or halogen. Such compounds exhibit hole transport properties as described in 1993 by Novo et al. in 1993 in Phys. Stat. Solidi(B), volume 177, page 223, and by Van der Auweraer et al. in Journal of Physical Chemistry, volume 97, page 8808. In addition such compounds form thermally stable amorphous layers with glass transition temperatures greater than  $100^\circ C$  as reported by Inada et al. in 1993 in Journal of Materials Chemistry, volume 3, pages 319-320. This combination of properties render such starburst compounds particularly interesting for use in organic electroluminescent devices as reported in 1996 by Inada et 20 al. in Mol. Cryst. Liq. Cryst., volume 280, pages 331-336, and in 1997 by Shirota et al. in Journal of Luminescence, volumes 72-74, pages 985-991.

## Aspects of the invention.

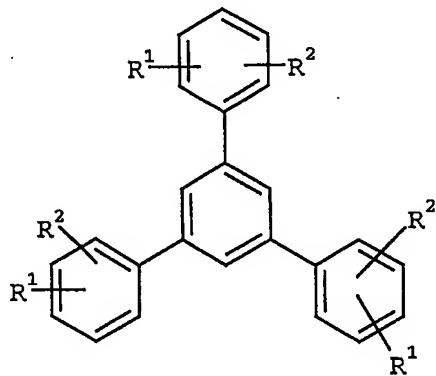
It is therefore an aspect of the present invention to provide a photovoltaic cell with a stable hole-conducting compound.

Further aspects and advantages of the invention will become apparent from the description hereinafter.

## Summary of the invention.

10 It has been surprisingly found that tris-1,3,5-amino-phenyl-benzene in a cationic form exhibited hole transporting properties which render them compatible with solid state photovoltaic cell configurations.

Aspects of the present invention are realized by a photovoltaic 15 device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):



wherein R<sup>1</sup> represents a -NR<sup>3</sup>R<sup>4</sup> group, wherein R<sup>3</sup> and R<sup>4</sup>, same or 20 different, represents a C<sub>2</sub>-C<sub>10</sub> alkyl group including the alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R<sup>2</sup> represents hydrogen, an alkyl group including a substituted alkyl group or halogen; and the 1,3,5-tris-aminophenyl-benzene compound is optionally in a cationic form.

25 Aspects of the present invention are realized by a process for preparing the above-mentioned photovoltaic device with at least one transparent electrode comprising the steps of: providing a support with a conductive layer as one electrode; coating the conductive layer on the support with a layer comprising the n-type 30 semiconductor with a bandgap of greater than 2.9 eV; coating the n-type semiconductor-containing layer with a solution or dispersion comprising the 1,3,5-tris-aminophenyl-benzene compound, or cation thereof, to provide after drying a layer comprising the 1,3,5-tris-

aminophenyl-benzene compound; and applying a conductive layer to the layer comprising the 1,3,5-tris-aminophenyl-benzene compound thereby providing a second electrode.

Preferred embodiments are disclosed in the dependent claims.

5

Detailed description of the invention.

#### Definitions

10 The term chalcogenide means a binary compound containing a chalcogen and a more electropositive element or radical. A chalcogen is an element from group IV of the periodic table including oxygen, sulphur, selenium, tellurium and polonium.

15 The term "support" means a "self-supporting material" so as to distinguish it from a "layer" which may be coated on a support, but which is itself not self-supporting. It also includes any treatment necessary for, or layer applied to aid, adhesion to the support.

20 The term continuous layer refers to a layer in a single plane covering the whole area of the support and not necessarily in direct contact with the support.

25 The term non-continuous layer refers to a layer in a single plane not covering the whole area of the support and not necessarily in direct contact with the support.

The term coating is used as a generic term including all means 25 of applying a layer including all techniques for producing continuous layers, such as curtain coating and doctor-blade coating, and all techniques for producing non-continuous layers such as screen printing, ink jet printing, flexographic printing.

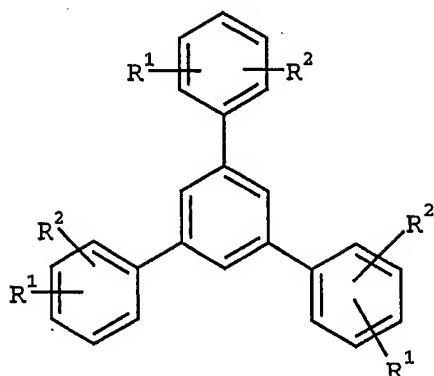
30 The abbreviation PEDOT represents poly(3,4-ethylenedioxy- thiophene).

The abbreviation PSS represents poly(styrenesulphonic acid) or poly(styrenesulphonate).

#### Photovoltaic devices

35

Aspects of the present invention are realized by a photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):



wherein R<sup>1</sup> represents a -NR<sup>3</sup>R<sup>4</sup> group, wherein R<sup>3</sup> and R<sup>4</sup>, same or different, represents a C<sub>2</sub>-C<sub>10</sub> alkyl group including the alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R<sup>2</sup> represents hydrogen, an alkyl group including a substituted alkyl group or halogen; and the 1,3,5-tris-aminophenyl-benzene compound is optionally in a cationic form.

Photovoltaic devices, according to the present invention, can be of two types: the regenerative type which converts light into electrical power leaving no net chemical change behind in which current-carrying electrons are transported to the anode and the external circuit and the holes are transported to the cathode where they are oxidized by the electrons from the external circuit and the photosynthetic type in which there are two redox systems one reacting with the holes at the surface of the semiconductor electrode and one reacting with the electrons entering the counter-electrode, for example, water is oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. In the case of the regenerative type of photovoltaic cell, as exemplified by the solid state Graetzel cell. The charge transporting process can be ionic or electronic.

Such regenerative photovoltaic devices can have a variety of internal structures in conformity with the end use. Conceivable forms are roughly divided into two types: structures which receive light from both sides and those which receive light from one side. An example of the former is a structure made up of a transparently conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer and a transparent counter electrode electrically conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer having interposed therebetween a photosensitive layer and a charge transporting layer. Such devices preferably have their sides sealed with a polymer or an adhesive to prevent deterioration or volatilization of the inside substances. The external circuit connected to the

electrically-conductive substrate and the counter electrode via the respective leads is well-known.

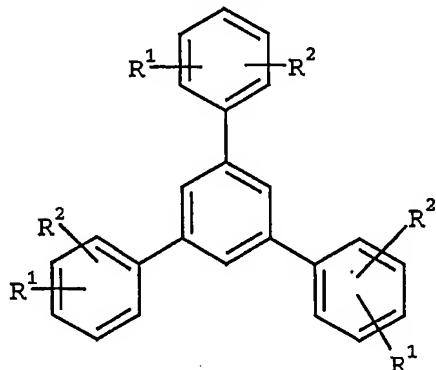
According to a first embodiment of the photovoltaic device, according to the present invention, the photovoltaic device 5 comprises a single layer system.

According to a second embodiment of the photovoltaic device, according to the present invention, the photovoltaic device comprises a configuration in which the n-type semiconductor with a band-gap of greater than 2.9 eV is contiguous with the 1,3,5-tris-10 aminophenyl-benzene compound according to formula (I) or in which a spectral sensitizer is sandwiched between the n-type semiconductor with a band-gap of greater than 2.9 eV and the 1,3,5-tris-aminophenyl-benzene compound according to formula (I).

15

### 1,3,5-Tris-aminophenyl-benzene compounds

A photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):

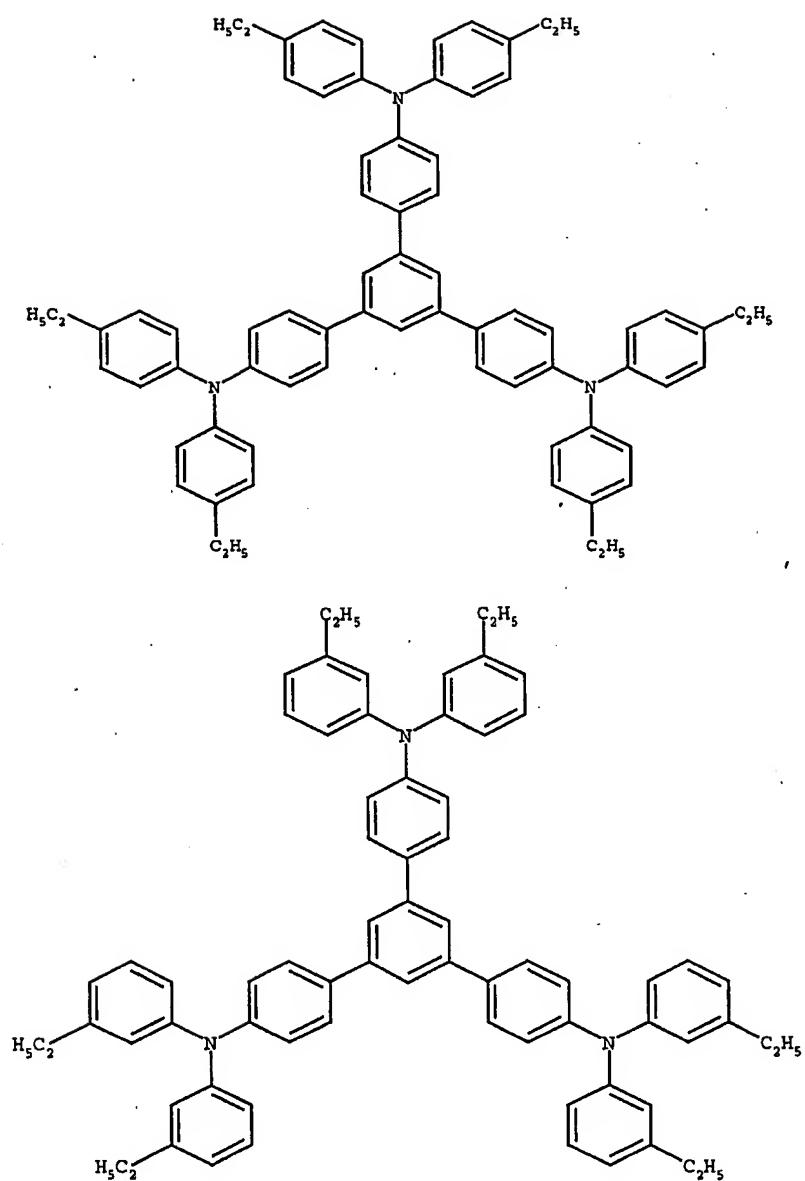


20

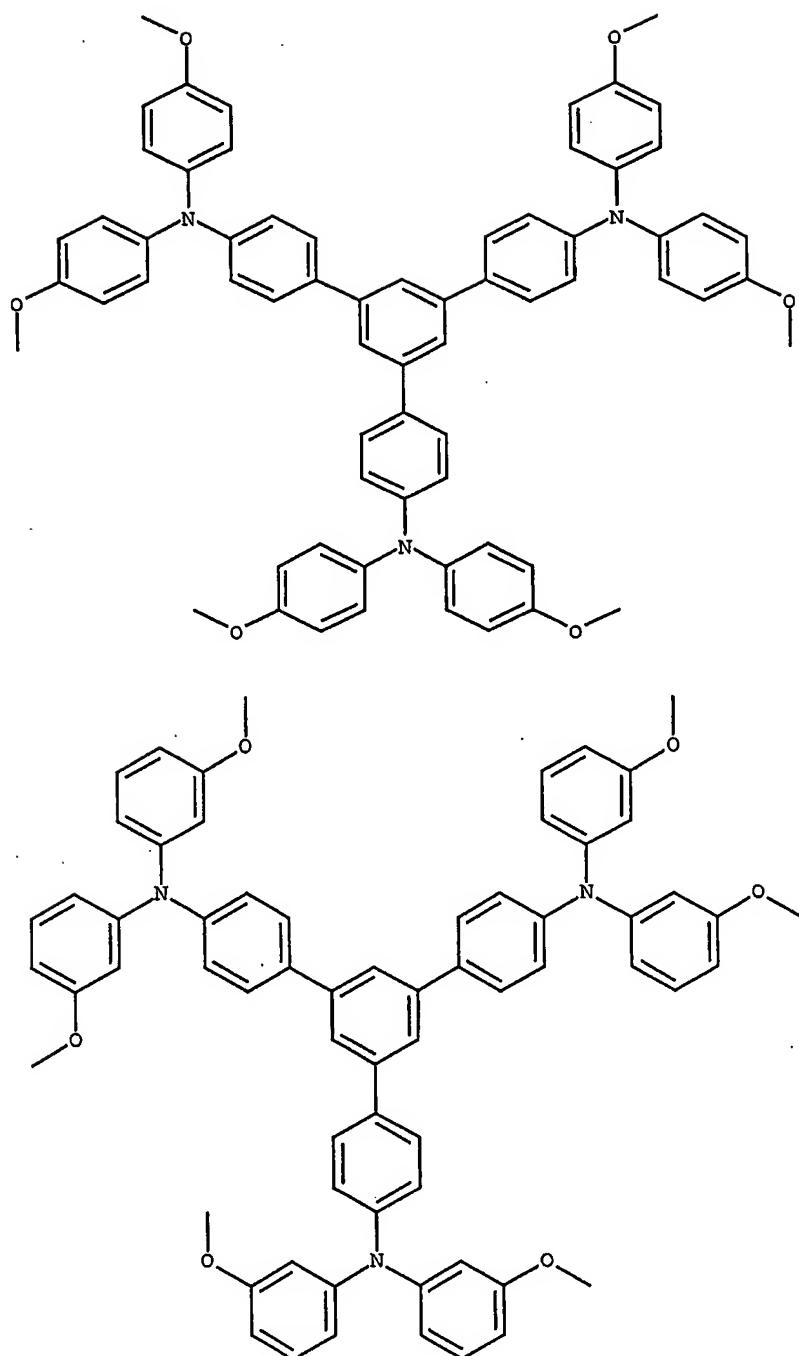
wherein R¹ represents a -NR³R⁴ group, wherein R³ and R⁴, same or different, represents a C₂-C₁₀ alkyl group including the alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R² represents hydrogen, an alkyl group including 25 a substituted alkyl group or halogen; and the 1,3,5-tris-aminophenyl-benzene compound is optionally in a cationic form.

According to a third embodiment of the photovoltaic device, according to the present invention, the 1,3,5-tris-aminophenyl-benzene compound represented by formula (I) is selected from the 30 group consisting of:

7

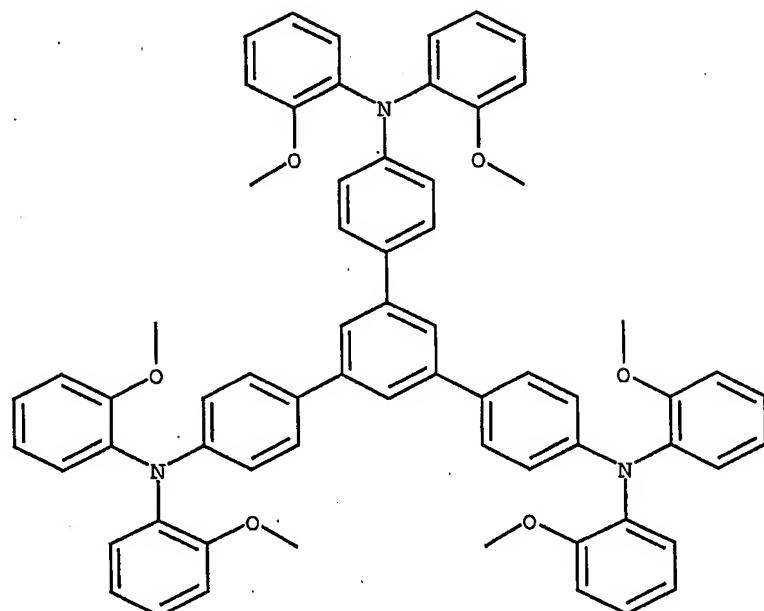


5



5 and

9



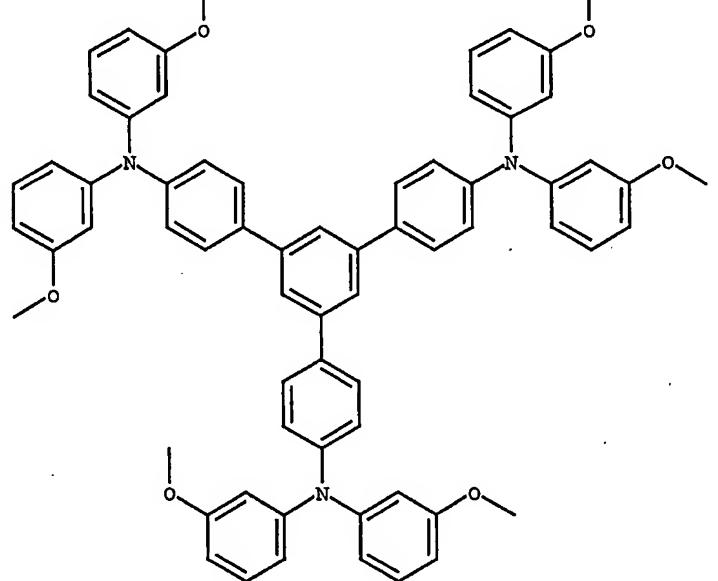
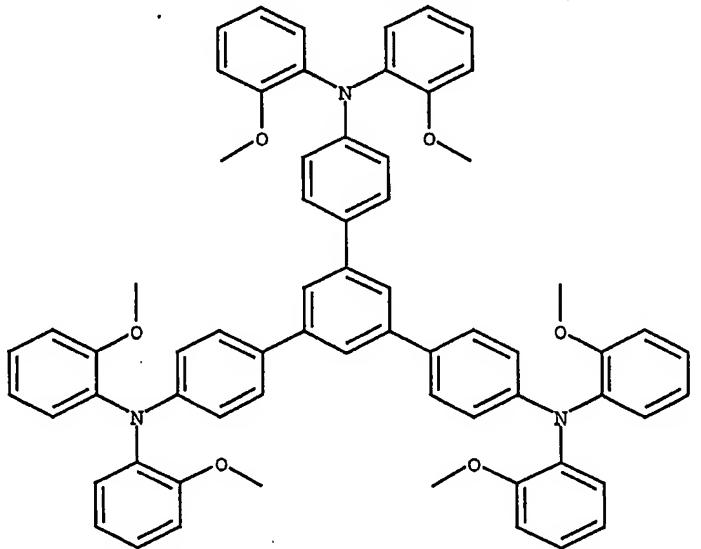
or the cations thereof.

Suitable 1,3,5-Tris-aminophenyl-benzene (TAPB) compounds, according to the present invention, include:

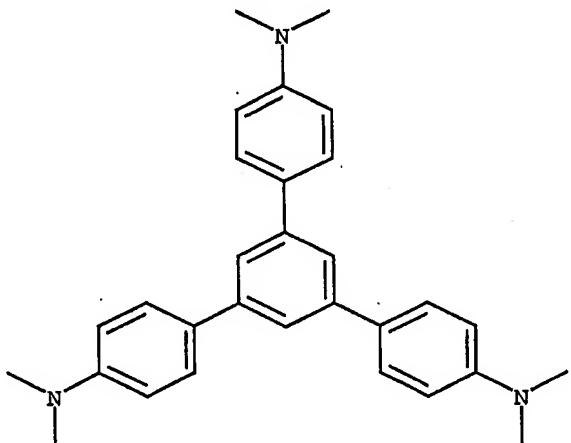
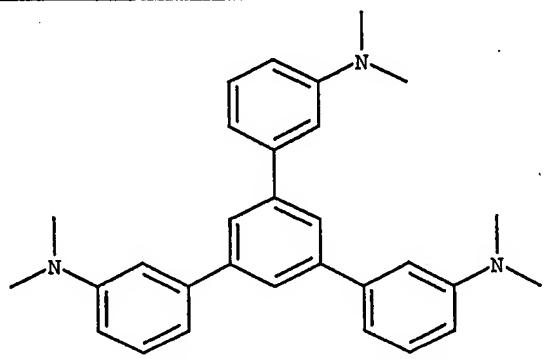
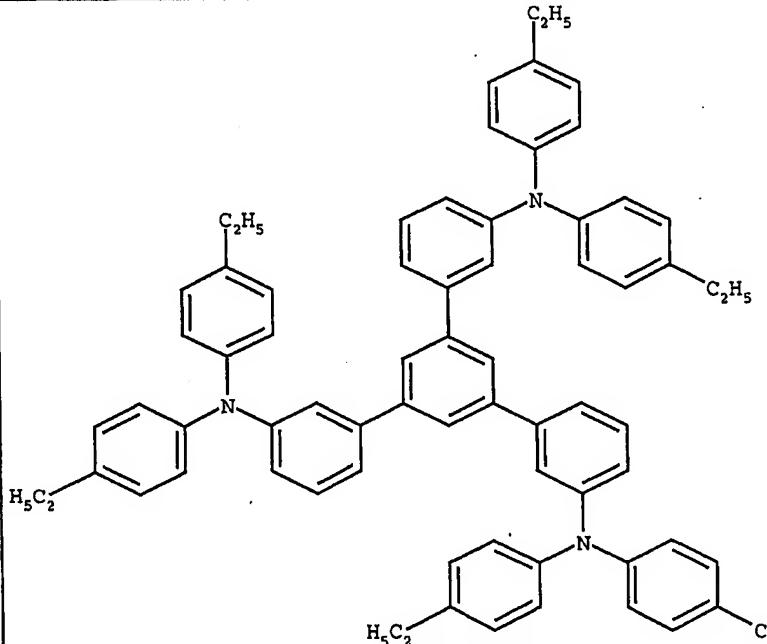
5

TAPB compound		$E^{1/2}_{ox}$ in MeCN vs sce [V]*
TAPB01		0.86

TAPB02		0.90
TAPB03		0.937

TAPB04		0.70
TAPB05		

TAPB06		0.73
TAPB07		0.855
TAPB08		0.810

TAPB09		
TAPB10		0.805
TAPB11		0.900

TAPB12		0.802
TAPB13		-
TAPB14		-

\* reference ferrocene: 0.430 V

TAPB01 has a glass transition temperature of 107°C.

Cations of 1,3,5-tris-aminophenyl-benzene compounds according to formula (I) can be prepared by oxidation of the particular 1,3,5-tris-aminophenyl-benzene compound with an oxidizing agent such as  $N(p\text{-C}_6\text{H}_4\text{Br})_3\text{SbCl}_6$ .

## n-type Semiconductors

According to a fourth embodiment of the photovoltaic device, according to the present invention, the n-type semiconductor has a bandgap of less than 6.0 eV.

According to a fifth embodiment of the photovoltaic device, according to the present invention, the n-type semiconductor is selected from the group consisting of titanium oxides, tin oxides, niobium oxides, tantalum oxides, tungsten oxides and zinc oxides.

10 The n-type semiconductor may be porous or non-porous, although non-porous n-type semiconductors are preferred.

According to a sixth embodiment of the photovoltaic device, according to the present invention, the n-type semiconductor is titanium dioxide.

15

## Spectral sensitization of n-type semiconductor layers

According to a seventh embodiment of the photovoltaic device, according to the present invention, the photovoltaic device further 20 contains at least one spectral sensitizer.

According to an eighth embodiment of the photovoltaic device, according to the present invention, the photovoltaic device further contains at least one spectral sensitizer selected from the group consisting of metal chalcogenide nano-particles with a band-gap of 25 less than 2.9 eV and greater than 1.5 eV, organic dyes and metallo-organic dyes.

According to a ninth embodiment of the photovoltaic device, according to the present invention, the photovoltaic device further contains at least one spectral sensitizer selected from the group 30 consisting of metal oxides, metal sulphides and metal selenides.

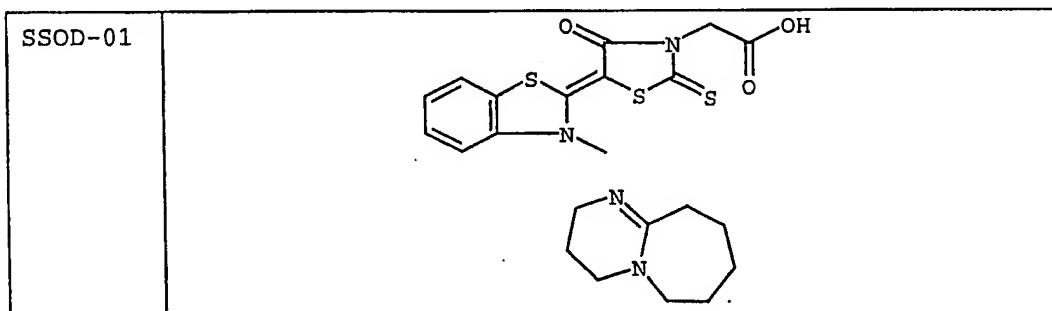
According to a tenth embodiment of the photovoltaic device, according to the present invention, the photovoltaic device further contains one or more metal sulphides nano-particles with a band-gap of less than 2.9 eV and greater than 1.5 eV.

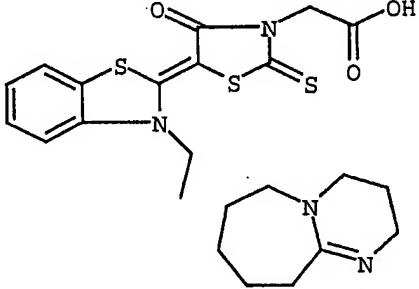
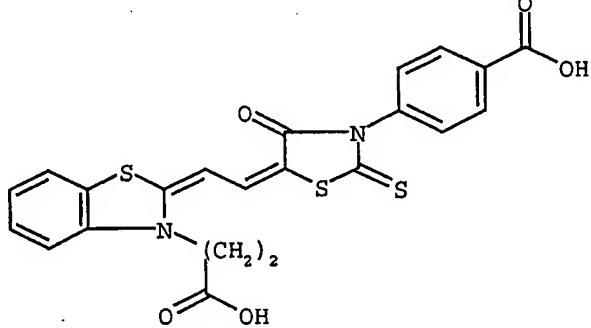
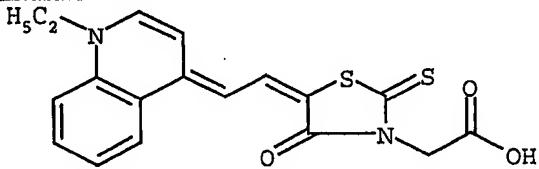
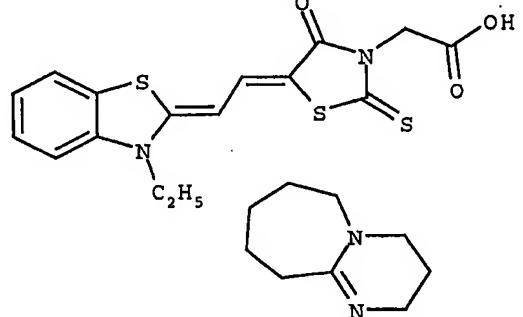
35 According to an eleventh embodiment of the photovoltaic device, according to the present invention, the photovoltaic device further contains one or more metal chalcogenide nano-particles selected from the group consisting of lead sulphide, bismuth sulphide, cadmium sulphide, silver sulphide, antimony sulphide, 40 indium sulphide, copper sulphide, cadmium selenide, copper selenide, indium selenide and cadmium telluride.

Vogel et al. in 1990 in Chemical Physics Letters, volume 174, page 241, herein incorporated by reference, reported the sensitization of highly porous  $TiO_2$  with in-situ prepared quantum size  $CdS$  particles (40-200Å), a photovoltage of 400 mV being achieved with visible light and high photon to current efficiencies of greater than 70% being achieved at 400 nm and an energy conversion efficiency of 6.0% under monochromatic illumination with  $\lambda = 460$  nm. In 1994 Hoyer et al. reported in Applied Physics, volume 66, page 349, that the inner surface of a porous titanium dioxide film could be homogeneously covered with isolated quantum dots.

EP-A 1 176 646, herein incorporated by reference, discloses a solid state p-n heterojunction comprising an electron conductor and a hole conductor, characterized in that it further comprises a sensitizing semiconductor, said sensitizing semiconductor being located at an interface between said electron conductor and said hole conductor; and its application in a solid state sensitized photovoltaic cell. In a preferred embodiment the sensitizing semiconductor is in the form of particles adsorbed at the surface of said electron conductor and in a further preferred embodiment the sensitizing semiconductor is in the form of quantum dots, which according to a particularly preferred embodiment are particles consisting of  $PbS$ ,  $CdS$ ,  $Bi_2S_3$ ,  $Sb_2S_3$ ,  $Ag_2S$ ,  $InAs$ ,  $CdTe$ ,  $CdSe$  or  $HgTe$  or solid solutions of  $HgTe/CdTe$  or  $HgSe/CdSe$ .

Suitable spectrally sensitizing organic dyes (SSOD) include cyanine, merocyanine and anionic dyes, such as:



SSOD-02	
SSOD-03	
SSOD-04	 $\text{H}_5\text{C}_2-\text{N}(\text{C}_2\text{H}_5)_2$
SSOD-05	

Suitable spectrally sensitizing metalloc-organic dyes allowing for broad absorption of the solar spectrum include:

	chemical name
Ruthenium 470, a ruthenium dye from Solaronix	tris(2,2'bipyridyl-4,4' dicarboxylato)ruthenium (II) dichloride
Ruthenium 505, a ruthenium dye from Solaronix	cis-bis(isocyanato) (2,2'bipyridyl-4,4' dicarboxylato) ruthenium (II)
Ruthenium 535 (previously known as SRS-HQ, N3), a ruthenium dye from Solaronix	cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)
Ruthenium 535 bis-TBA (previously known as MRS-HQ, N719, dye salt) a ruthenium dye from Solaronix	cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium
Ruthenium 620 "Black Dye", a ruthenium dye from Solaronix	(anion only) tris(isothiocyanato)-ruthenium(II)-2,2':6',2"-terpyridine-4,4',4"-tricarboxylic acid

#### Process for preparing a photovoltaic device

Aspects of the present invention are realized by a process for preparing a photovoltaic device, according to the present invention, with at least one transparent electrode comprising the steps of: providing a support with a conductive layer as one electrode; coating the conductive layer on the support with a layer comprising the n-type semiconductor with a bandgap of greater than 2.9 eV; coating the n-type semiconductor-containing layer with a solution or dispersion comprising the 1,3,5-tris-aminophenyl-benzene compound, or cation thereof, to provide after drying a layer comprising the 1,3,5-tris-aminophenyl-benzene compound; and

applying a conductive layer to the layer comprising the 1,3,5-tris-aminophenyl-benzene compound thereby providing a second electrode.

According to a first embodiment of the process, according to the present invention, the solution or dispersion of the 1,3,5-tris-aminophenyl-benzene compound according to formula (I) or cation thereof further contains a binder.

According to a second embodiment of the process, according to the present invention, the solution or dispersion of the 1,3,5-tris-aminophenyl-benzene compound according to formula (I) or cation thereof further contains an electrolyte. Suitable electrolytes include  $\text{Li}[(\text{CF}_3\text{SO}_2)_2\text{N}]$  and lithium trifluoromethanesulphonate (lithium triflate).

According to a third embodiment of the process, according to the present invention, the process further comprises the step of applying a solution or dispersion of a spectral sensitizer directly to the n-type semiconductor layer.

#### Support

Supports for use according to the present invention include polymeric films, silicon, ceramics, oxides, glass, polymeric film reinforced glass, glass/plastic laminates, metal/plastic laminates, paper and laminated paper, optionally treated, provided with a subbing layer or other adhesion promoting means to aid adhesion to the layer configuration, according to the present invention.

Suitable polymeric films are poly(ethylene terephthalate), poly(ethylene naphthalate), polystyrene, polyethersulphone, polycarbonate, polyacrylate, polyamide, polyimides, cellulose triacetate, polyolefins and poly(vinylchloride), optionally treated by corona discharge or glow discharge or provided with a subbing layer.

#### Industrial application

Layers of nano-porous metal oxide semiconductors with a band-gap of greater than 2.9 eV prepared according the process, according to the present invention, can be used in both regenerative and photosynthetic photovoltaic devices.

The invention is illustrated hereinafter by way of reference and invention photovoltaic devices. The percentages and ratios given in these examples are by weight unless otherwise indicated.

Spiro-OMeTAD from SOLARONIX with the chemical name 2,2'7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene was used as a reference material to check if the basic recipe and the configuration of the cell were in order.

#### EXAMPLE 1

Photovoltaic devices with solid state organic hole conductor and  
10 high temperature sintered nano-porous TiO<sub>2</sub>.

Photovoltaic devices 1 to 3 were prepared by the following procedure:

15 Preparation of the front electrode:

A glass plate (2 x 7 cm<sup>2</sup>) coated with conductive SnO<sub>2</sub>:F (Pilkington TEC15/3) with a surface conductivity of ca. 15 Ohm/square was ultrasonically cleaned in isopropanol for 5 minutes  
20 and then dried.

A small strip of SnO<sub>2</sub>:F was removed to prevent short circuit. The glass electrode was partially covered with glass on the long side and a dense non-porous hole blocking titanium dioxide layer applied by spray pyrolysis of an ethanolic solution of di-  
25 isopropoxy titanium-bis (acetylacetone) in aerosol form as described by Kavan L. et al. In Electrochim. Acta (1995), 40(5), 643-52, herein incorporated by reference.

5 g of P25, a flame pyrolyzed nano-sized titanium dioxide with a mean particle size of 25 nm and a specific surface of 55 m<sup>2</sup>/g  
30 from DEGUSSA, was added to 15 mL of water followed by 1 mL of Triton X-100. The resulting titanium dioxide colloidal dispersion was cooled in ice and ultrasonically treated for 5 minutes. This dispersion was then doctor-blade coated onto the middle (0.7 x 4.5 cm<sup>2</sup>) of the electrode with the non-porous hole blocking titanium  
35 dioxide layer taped off at the borders. Nano-sized titanium dioxide dispersion-coated glass electrodes were heated at 450°C for 30 minutes then cooled to 150°C on a hot plate at 150°C for 10 minutes thereby yielding a nano-porous TiO<sub>2</sub> layer thickness of 2 µm. After cooling to 150°C, the nano-porous TiO<sub>2</sub> layer-coated glass electrode  
40 was immediately immersed in a 2 x 10<sup>-4</sup> M solution of the Ruthenium 535 bis-TBA dye (from SOLARONIX) for 15 to 17 hours, followed by rinsing with acetonitrile to remove the non-adsorbed dye and drying

at 50°C for several minutes. The front electrode thereby produced was immediately used in assembling a photovoltaic cell.

Coating with layers of hole transporting materials:

5

Solutions of the hole transporting materials were prepared as follows:

HTM solution 1:

10

60 mg (53.1  $\mu$ moles) of Spiro-OMeTAD was dissolved in 200  $\mu$ l chlorobenzene (Aldrich) by heating for 1 hour at 70°C. 10.5  $\mu$ l of a solution of 56.7  $\mu$ g N(p-C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>SbCl<sub>6</sub> (69.4 nmoles) (Aldrich) and 907  $\mu$ g Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] (3.16  $\mu$ moles) (Fluka) in acetonitrile were then 15 added to this solution to give a HTM solution 1 0.25M in Spiro-OMeTAD, 0.33mM in N(p-C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>SbCl<sub>6</sub> and 15mM in Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N].

HTM solution 2:

20 35 mg (35.8  $\mu$ moles) of TABP01 was dissolved in 200  $\mu$ l chlorobenzene (Aldrich). To this solution, 10.5  $\mu$ l of a solution of 56.7 mg N(p-C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>SbCl<sub>6</sub> (69.4 nmoles) (Aldrich) and 907 mg Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] (3.16  $\mu$ moles) (Fluka) in acetonitrile was then added to the solution to give to give a HTM solution 2 0.17M in TABP01, 0.33mM in 25 N(p-C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>SbCl<sub>6</sub> and 15mM in Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N].

HTM solution 3:

35.4 mg (35.8  $\mu$ moles) of TABP03 was dissolved in 200  $\mu$ l 30 chlorobenzene (Aldrich). To this solution, 10.5  $\mu$ l of a solution of 56.7 mg N(p-C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>SbCl<sub>6</sub> (69.4 nmoles) (Aldrich) and 907 mg Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] (3.16  $\mu$ moles) (Fluka) in acetonitrile was then added to the solution to give to give a HTM solution 2 0.17M in TABP03, 0.33mM in N(p-C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>SbCl<sub>6</sub> and 15mM in Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N].

35

N(p-C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>SbCl<sub>6</sub> oxidized the charge transport compound to its cationic salt, Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] acting as an electrolyte. Sufficient N(p-C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>SbCl<sub>6</sub> was present to ensure that the oxidation process went to completion as determined spectrophotometrically by 40 monitoring, in the case of TABP01, the 397 nm, 695 nm and 772 nm peaks of the cationic state in analogy to the absorption spectrum reported in 1994 by Bonvoisin et al. in Journal of Physical

Chemistry, volume 98, pages 5052-5057. Bonvoisin et al. reported that cyclic voltammetry and coulometry on TABP01 showed a unique, reversible, oxidation wave corresponding to a three-electron process, which was accompanied by the appearance of three bands at 397 nm, 695 nm and 772 nm respectively, corresponding to the tri-cation chromophore. TABP01 and TABP03 appear to be oxidizable to their tri-cations i.e. all three nitrogens in the molecule are oxidizable, whereas in the case of Spiro-OMeTAD only two of the four nitrogens appear to be oxidizable.

10 The front electrode was placed on the spincoater, the cover was closed and a flow of Argon was fed in for 2 minutes. About 150  $\mu$ l of solution 1 was then dropped on the front electrode so as to cover the whole area. After waiting for 30 to 60 s for the drop to spread, the spincoater was again closed and again Argon flow was 15 fed in for 1 minute. It took 5 s for the spincoater to accelerate to 1000 rpm at which speed the solution was allowed to spin for 30 minutes.

16 The front electrode coated with the charge transport compound was then dried in the dark under Argon at 25°C for 30 minutes 20 followed by drying in a vacuum exicator for a further 30 minutes in dark. Finally a gold electrode was evaporated on top.

21 Measurements were only carried out after the photovoltaic device had stabilized in the dark at 25°C, which took between 1 and 24 hours. The same procedure was carried out for all six solutions. 25 This resulted in PV devices 1, 2 and 3.

#### Photovoltaic device characterisation

26 The photovoltaic device configuration is shown in Figure 1.

27 The cell was irradiated with a Steuernagel Solar Constant 575 solar simulator with a metal halide 1 AM light source. The simulator was adjusted to about 1 sunequivalent. The electricity generated was recorded with a Type 2400 SMU Keithley electrometer in the voltage range -1 to +1 volt.

32 Table 1 lists the short circuit current (I<sub>sc</sub>) and open circuit voltage (V<sub>oc</sub>) for the devices. The active area was 0.14 cm<sup>2</sup>.

Table 1:

photovoltaic device	hole transporting material	I <sub>sc</sub> (μA/cm <sup>2</sup> )	V <sub>oc</sub> (mV)
1 (ref.)	Spiro-OMeTAD	2880	795
2 (inv.)	TAPB01	11	585
3 (inv.)	TAPB03	4	475

Photovoltaic devices 2 and 3 with 1,3,5-tris-aminophenyl-benzene compounds TAPB01 and TAPB03 in a tri-cationic form and heat sintered titanium dioxide exhibit photovoltaic effects exhibit photovoltaic effects.

## EXAMPLE 2

10

Photovoltaic devices with solid state organic hole conductor and high pressure sintered nano-porous TiO<sub>2</sub>

Photovoltaic devices 4 to 6 were prepared by the following 15 procedure:

Photovoltaic devices 4 to 6 were prepared as described for Photovoltaic devices 1 to 3, except that nano-titanium dioxide dispersion-coated glass electrode was first dried at 110°C for 5 20 minutes, then, after cooling to room temperature, a pressure of 500 bars was applied for 5 seconds. This pressure sintered coating was then heated to 150°C, immediately immersed in a  $2 \times 10^{-4}$  M solution of the Ruthenium 535 bis-TBA dye and then washed and dried as described for Photovoltaic devices 1 to 3.

25

Photovoltaic device 7 was prepared by the following procedure:

A  $2 \times 7$  cm<sup>2</sup> piece of ITO-coated (from IST) with a surface resistivity of 70 Ohm/square was cleaned by rinsing in ethanol and 30 ozone treatment. The electrode was partially covered with adhesive tape and put in an electron-beam apparatus. It was placed overnight in a vacuum with continuous pumping and the non-porous TiO<sub>2</sub> was applied locally to the substrate. After the deposition, the vacuum was released and the sample was ready to use.

35 5 g of DEGUSSA P25 titanium dioxide nano-particles was added to 15 mL of water and the resulting titanium dioxide colloidal dispersion cooled in ice and ultrasonically treated for 5 minutes.

This dispersion was then doctor-blade-coated onto the middle ( $0.7 \times 4.5 \text{ cm}^2$ ) of the non-porous hole blocking titanium dioxide layer taped off at the borders.

The coated PET electrode with the nano titanium dioxide dispersion was first dried at  $110^\circ\text{C}$  for 5 minutes, then, after cooling to room temperature, a pressure of 500 bars was applied for 5 seconds. This pressure sintered coating was then heated to  $150^\circ\text{C}$ , immediately immersed in a  $2 \times 10^{-4} \text{ M}$  solution of the Ruthenium 535 dye and the procedure described for Photovoltaic devices 1 to 3 followed. Finally layers of Spiro-OMeTAD and gold were applied as described for Photovoltaic device 1.

Table 2 lists the results for the different hole transporting materials with pressure sintered  $\text{TiO}_2$  on a glass electrode and on an ITO-PET electrode.

15

Table 2:

Photovoltaic device	Substrate	hole transporting material	Isc ( $\mu\text{A}/\text{cm}^2$ )	Voc (mV)
4 (ref.)	Glass/SnO <sub>2</sub>	Spiro-OMeTAD	20	735
5 (inv.)	Glass/SnO <sub>2</sub>	TAPB01	0.66	215
6 (inv.)	Glass/SnO <sub>2</sub>	TAPB03	0.71	385
7 (ref.)	PET/ITO	Spiro-OMeTAD	5	585

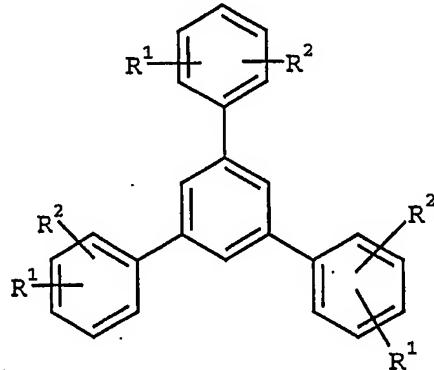
Photovoltaic devices 5 and 6 with 1,3,5-tris-aminophenyl-benzene compounds TAPB01 and TAPB03 in a tri-cationic form and pressure sintered titanium dioxide exhibit photovoltaic effects, which are much closer to the performance of the reference photovoltaic device with Spiro-OMeTAD than for photovoltaic devices with heat sintered titanium dioxide.

25

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

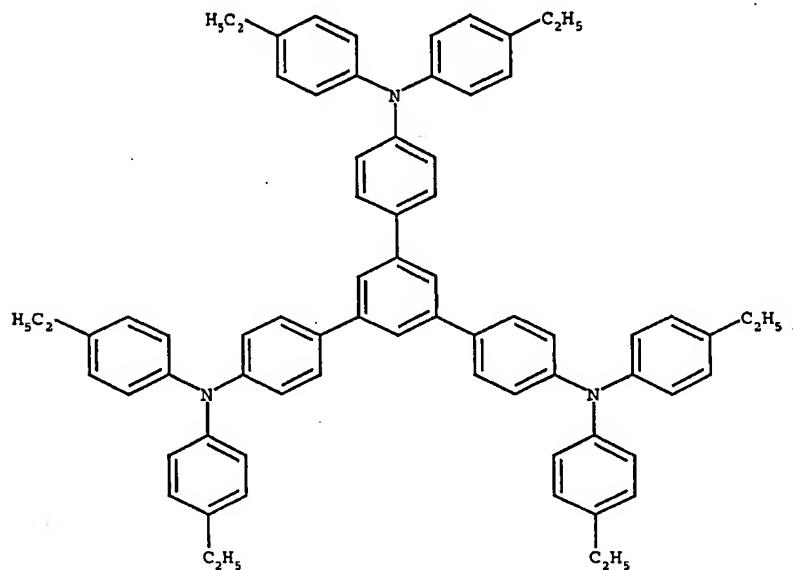
## CLAIMS

1. A photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):

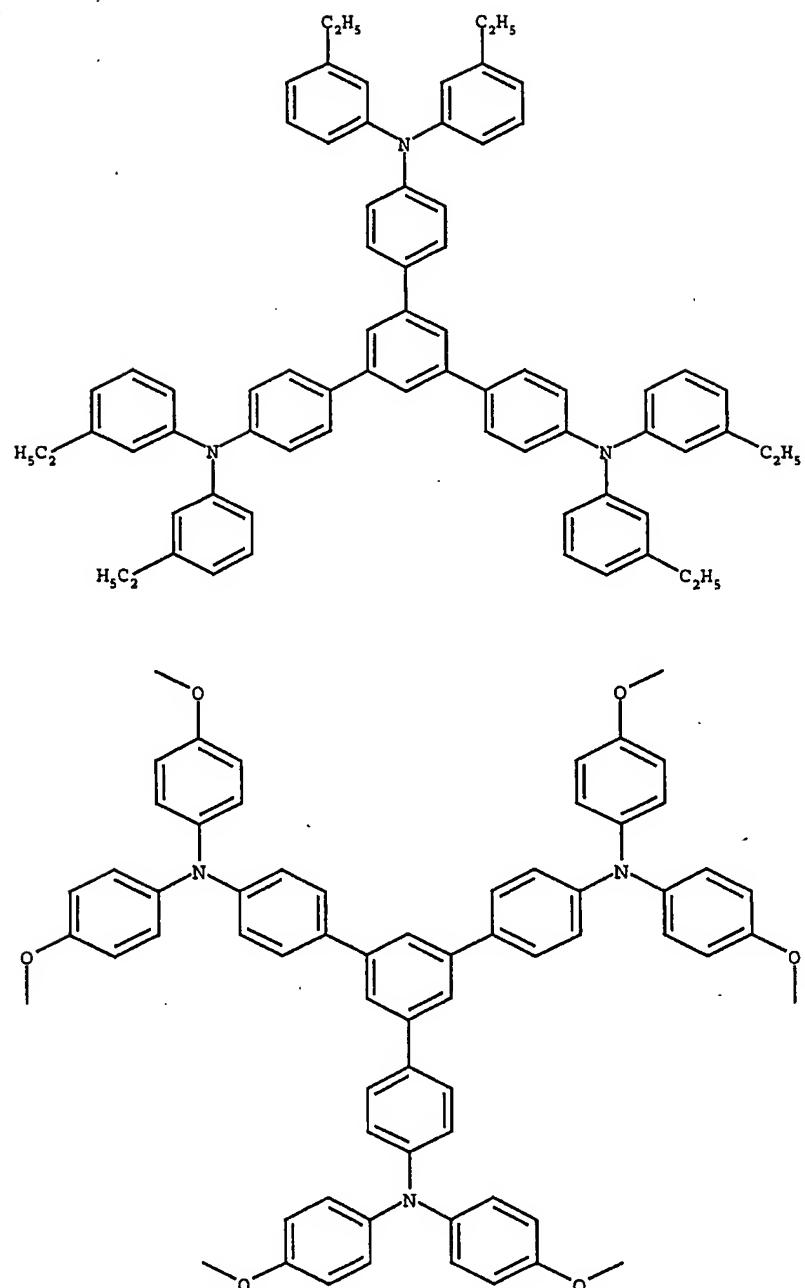


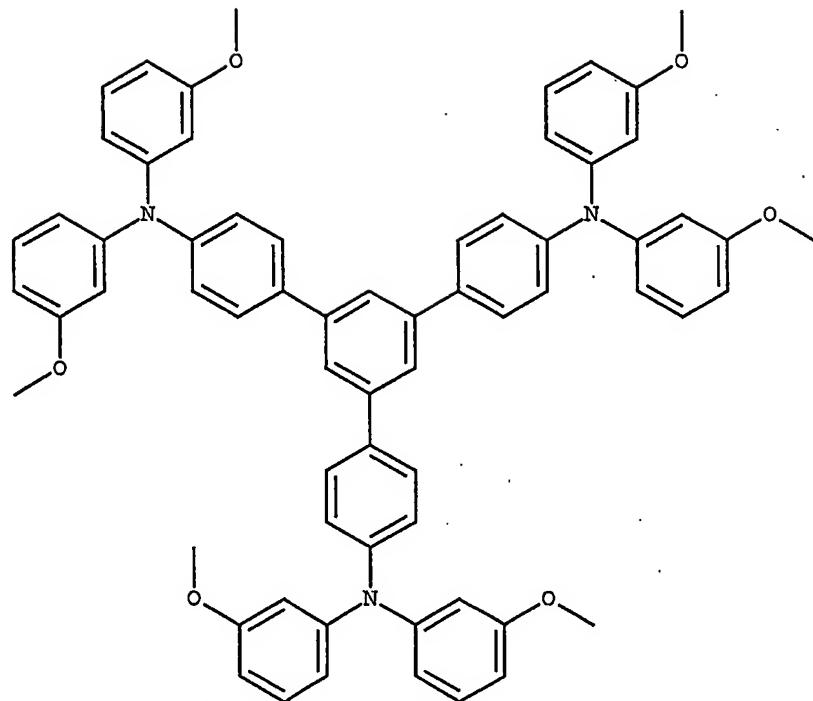
wherein R<sup>1</sup> represents a -NR<sup>3</sup>R<sup>4</sup> group, wherein R<sup>3</sup> and R<sup>4</sup>, same or different, represents a C<sub>2</sub>-C<sub>10</sub> alkyl group including said alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R<sup>2</sup> represents hydrogen, an alkyl group including a substituted alkyl group or halogen; and said 1,3,5-tris-aminophenyl-benzene compound is optionally in a cationic form.

15 2. Photovoltaic device according to claim 1, wherein said 1,3,5-tris-aminophenyl-benzene compound represented by formula (I) is selected from the group consisting of:

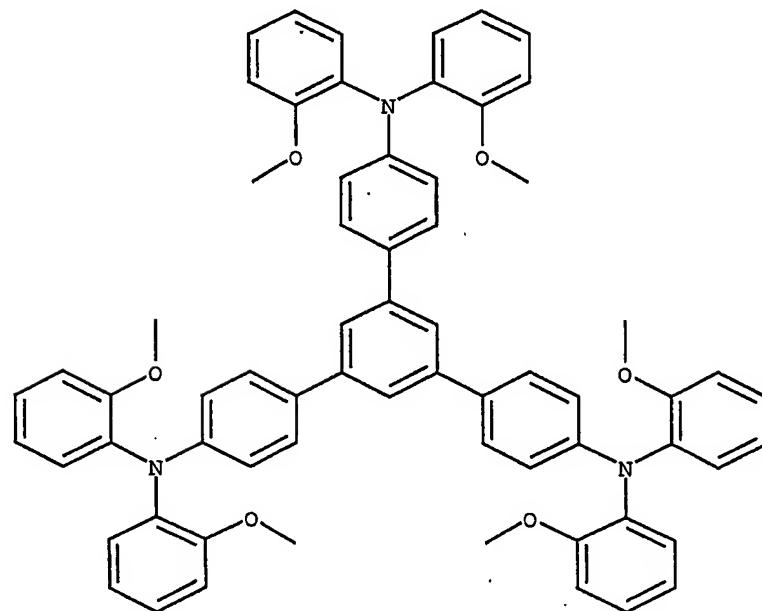


26





and

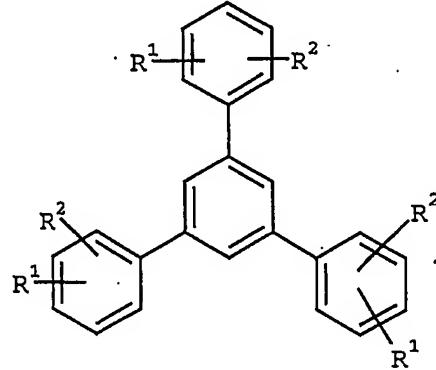


5 or the cations thereof.

3. Photovoltaic device according to claim 1, wherein said n-type semiconductor is selected from the group consisting of

titanium oxides, tin oxides, niobium oxides, tantalum oxides, tungsten oxides and zinc oxides.

4. Photovoltaic device according to claim 1, wherein said photovoltaic device further contains at least one spectral sensitizer.
5. Photovoltaic device according to claim 1, wherein said photovoltaic device further contains at least one spectral sensitizer selected from the group consisting of metal chalcogenide nano-particles with a band-gap of less than 2.9 eV, organic dyes and metallo-organic dyes.
10. Photovoltaic device according to claim 1, wherein said photovoltaic device further contains at least one spectral sensitizer selected from the group consisting of metal oxides, metal sulphides and metal selenides.
15. Photovoltaic device according to claim 1, wherein said photovoltaic device further contains at least one spectral sensitizer selected from the group consisting of metal oxides, metal sulphides and metal selenides.
20. A process for preparing a photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):



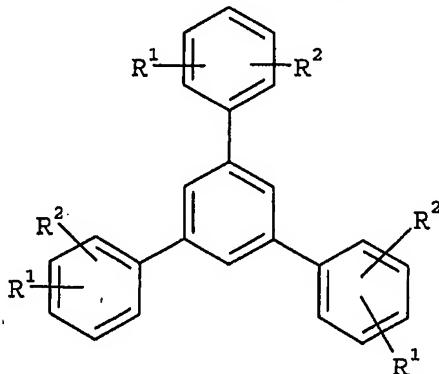
25. wherein R<sup>1</sup> represents a -NR<sup>3</sup>R<sup>4</sup> group, wherein R<sup>3</sup> and R<sup>4</sup>, same or different, represents a C<sub>2</sub>-C<sub>10</sub> alkyl group including said alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R<sup>2</sup> represents hydrogen, an alkyl group including a substituted alkyl group or halogen, and said 1,3,5-tris-aminophenyl-benzene compound is optionally in a cationic form, with at least one transparent electrode comprising the steps of: providing a support with a conductive layer as one electrode; coating said conductive layer on the support with a layer comprising said n-type semiconductor with a bandgap of

greater than 2.9 eV; coating said n-type semiconductor-containing layer with a solution or dispersion comprising said 1,3,5-tris-aminophenyl-benzene compound, or cation thereof, to provide after drying a layer comprising said 1,3,5-tris-aminophenyl-benzene compound; and applying a conductive layer to said layer comprising said 1,3,5-tris-aminophenyl-benzene compound thereby providing a second electrode.

## AMENDED CLAIMS

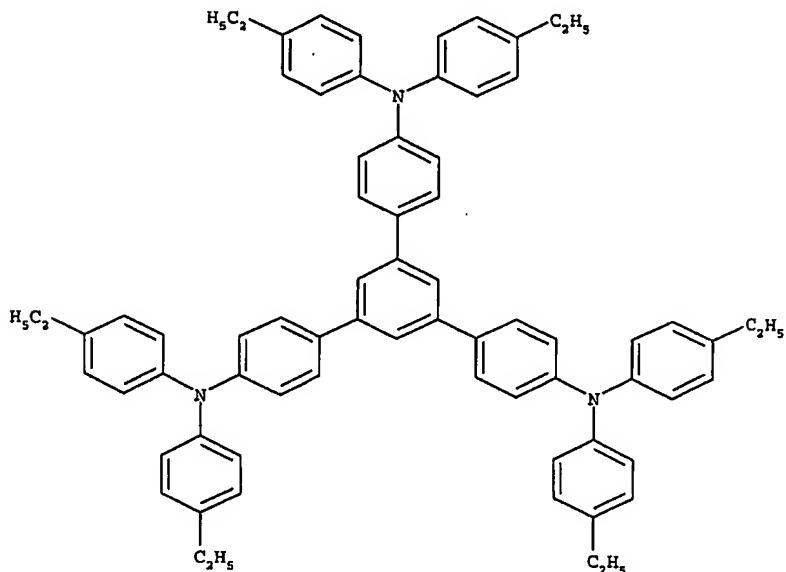
[received by the International Bureau on 14 August 2003 (14.08.03)  
 claims 1-7 replaced by claims 1-14 (9 pages)]

1. A photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):

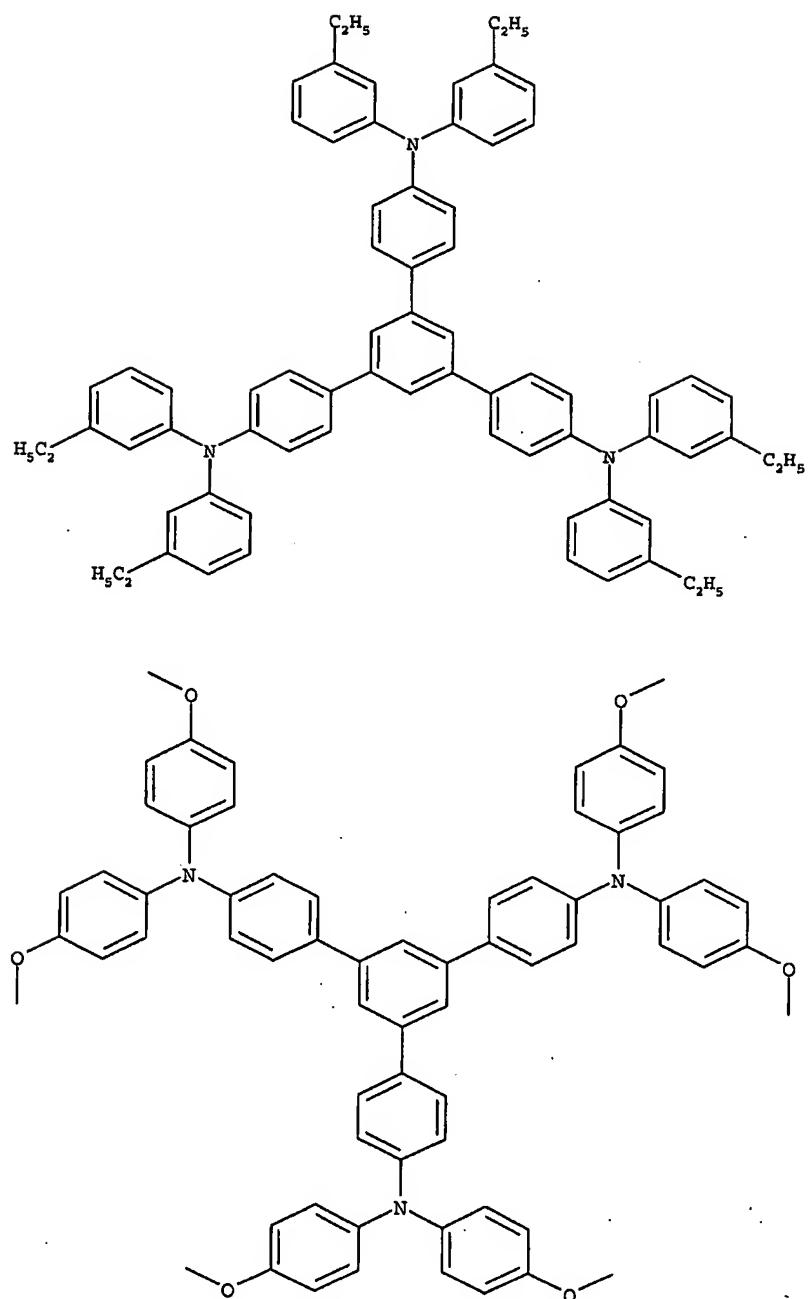


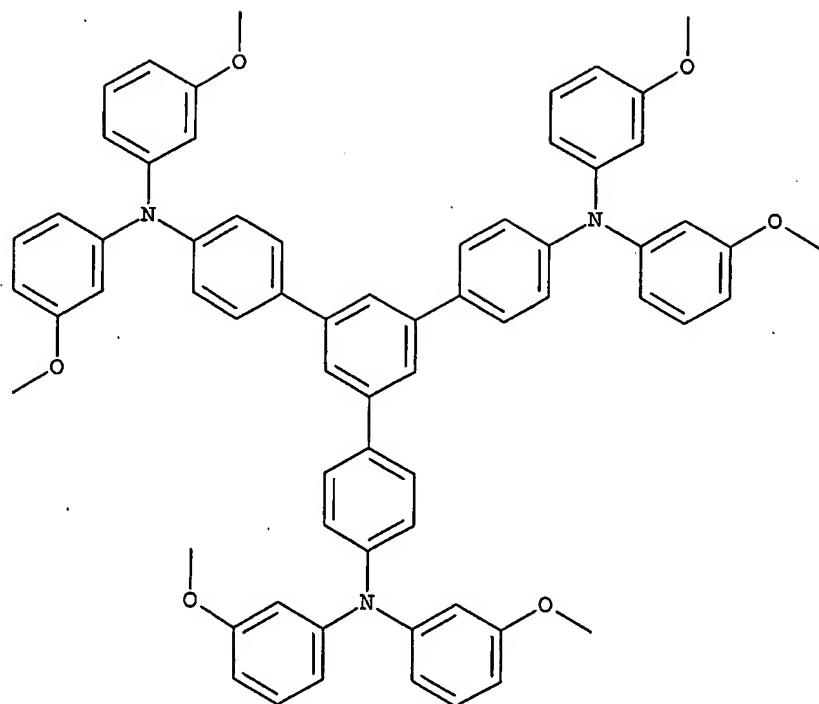
wherein R<sup>1</sup> represents a -NR<sup>3</sup>R<sup>4</sup> group, wherein R<sup>3</sup> and R<sup>4</sup>, same or different, represents a C<sub>2</sub>-C<sub>10</sub> alkyl group including said alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R<sup>2</sup> represents hydrogen, an alkyl group including a substituted alkyl group or halogen; and said 1,3,5-tris-aminophenyl-benzene compound is in a cationic form.

2. Photovoltaic device according to claim 1, wherein said 1,3,5-tris-aminophenyl-benzene compound represented by formula (I) is selected from the group consisting of the cations of:

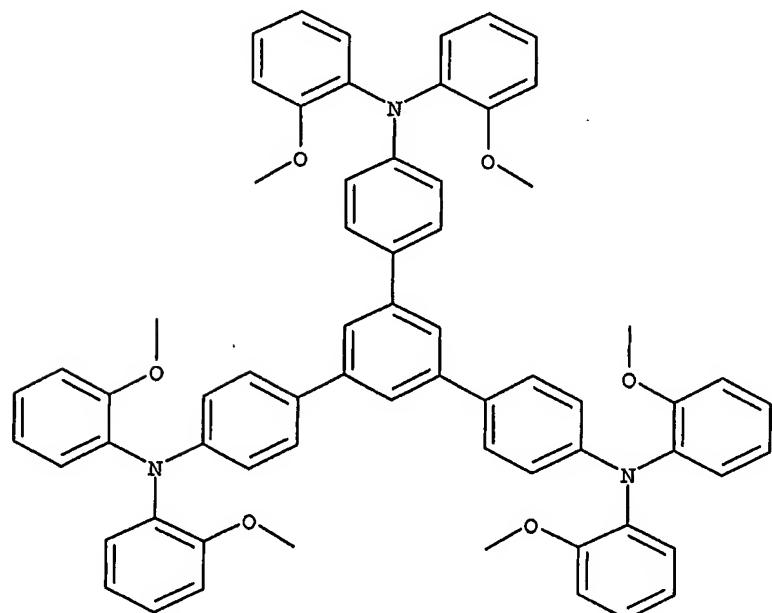


AMENDED SHEET (ARTICLE 19)





and



5

3. Photovoltaic device according to claim 1, wherein said n-type semiconductor is selected from the group consisting of titanium oxides, tin oxides, niobium oxides, tantalum oxides, tungsten oxides and zinc oxides.

10

**AMENDED SHEET (ARTICLE 19)**

4. Photovoltaic device according to claim 1, wherein said photovoltaic device further contains at least one spectral sensitizer.

5. Photovoltaic device according to claim 1, wherein said photovoltaic device further contains at least one spectral sensitizer selected from the group consisting of metal chalcogenide nano-particles with a band-gap of less than 2.9 eV, organic dyes and metallo-organic dyes.

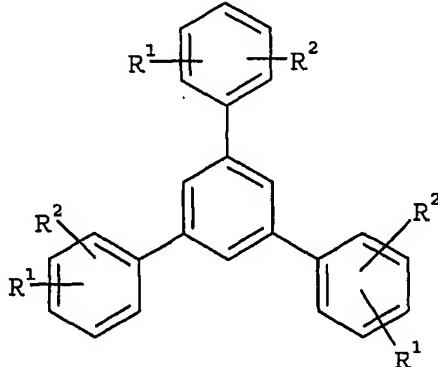
10

6. Photovoltaic device according to claim 1, wherein said photovoltaic device further contains at least one spectral sensitizer selected from the group consisting metal oxides, metal sulphides and metal selenides.

15

7. A process for preparing a photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):

20



25

wherein R<sup>1</sup> represents a -NR<sup>3</sup>R<sup>4</sup> group, wherein R<sup>3</sup> and R<sup>4</sup>, same or different, represents a C<sub>2</sub>-C<sub>10</sub> alkyl group including said alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R<sup>2</sup> represents hydrogen, an alkyl group including a substituted alkyl group or halogen, and said 1,3,5-tris-aminophenyl-benzene compound is in a cationic form, with at least one transparent electrode comprising the steps of:

30

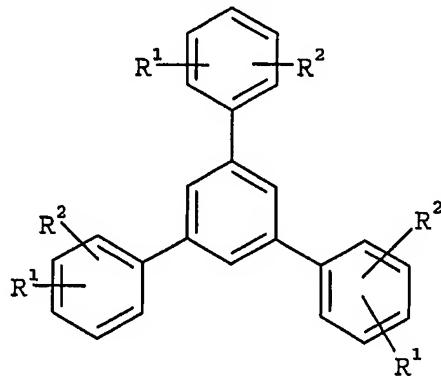
providing a support with a conductive layer as one electrode; coating said conductive layer on the support with a layer comprising said n-type semiconductor with a bandgap of greater than 2.9 eV; coating said n-type semiconductor-containing layer with a solution or dispersion comprising a cation of said 1,3,5-tris-aminophenyl-benzene compound to provide after drying a layer

**AMENDED SHEET (ARTICLE 19)**

comprising said 1,3,5-tris-aminophenyl-benzene compound; and applying a conductive layer to said layer comprising said cation of said 1,3,5-tris-aminophenyl-benzene compound thereby providing a second electrode.

5

8. A photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):

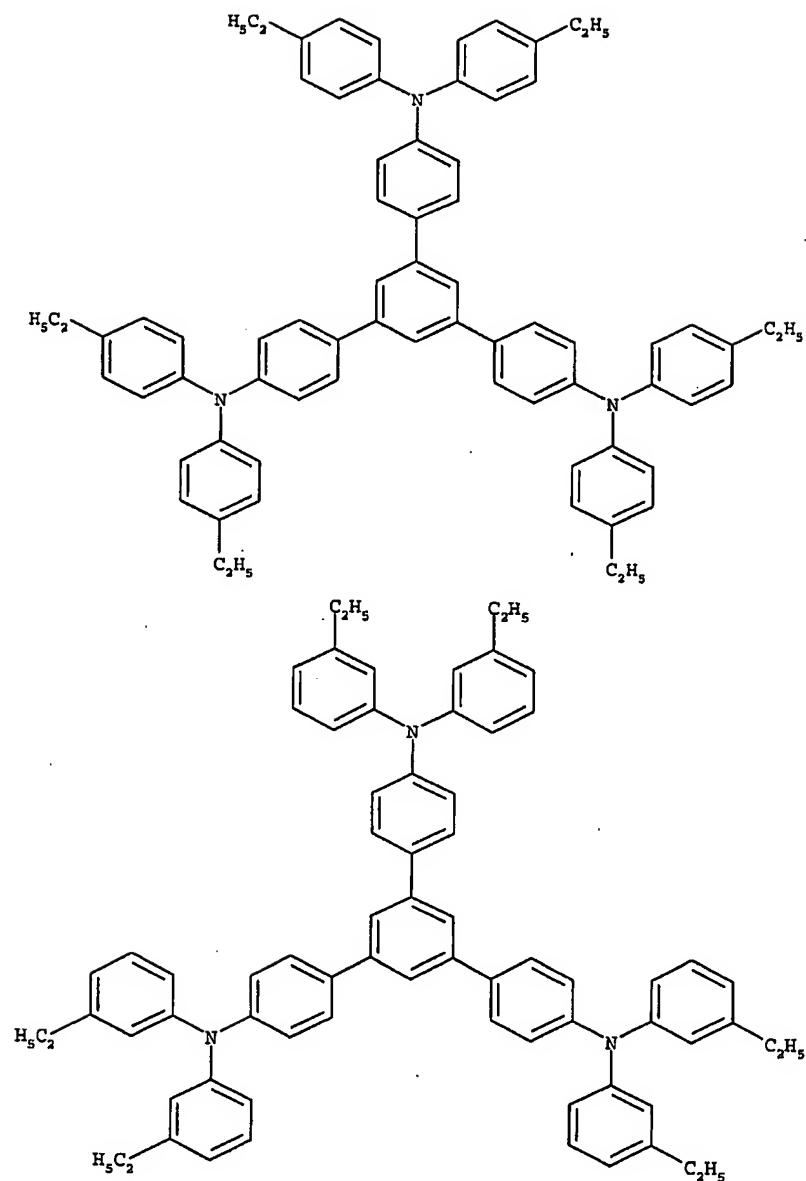


10 wherein R<sup>1</sup> represents a -NR<sup>3</sup>R<sup>4</sup> group, wherein R<sup>3</sup> and R<sup>4</sup>, same or different, represents a C<sub>2</sub>-C<sub>10</sub> alkyl group including said alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R<sup>2</sup> represents hydrogen, an alkyl group including a substituted alkyl group or halogen.

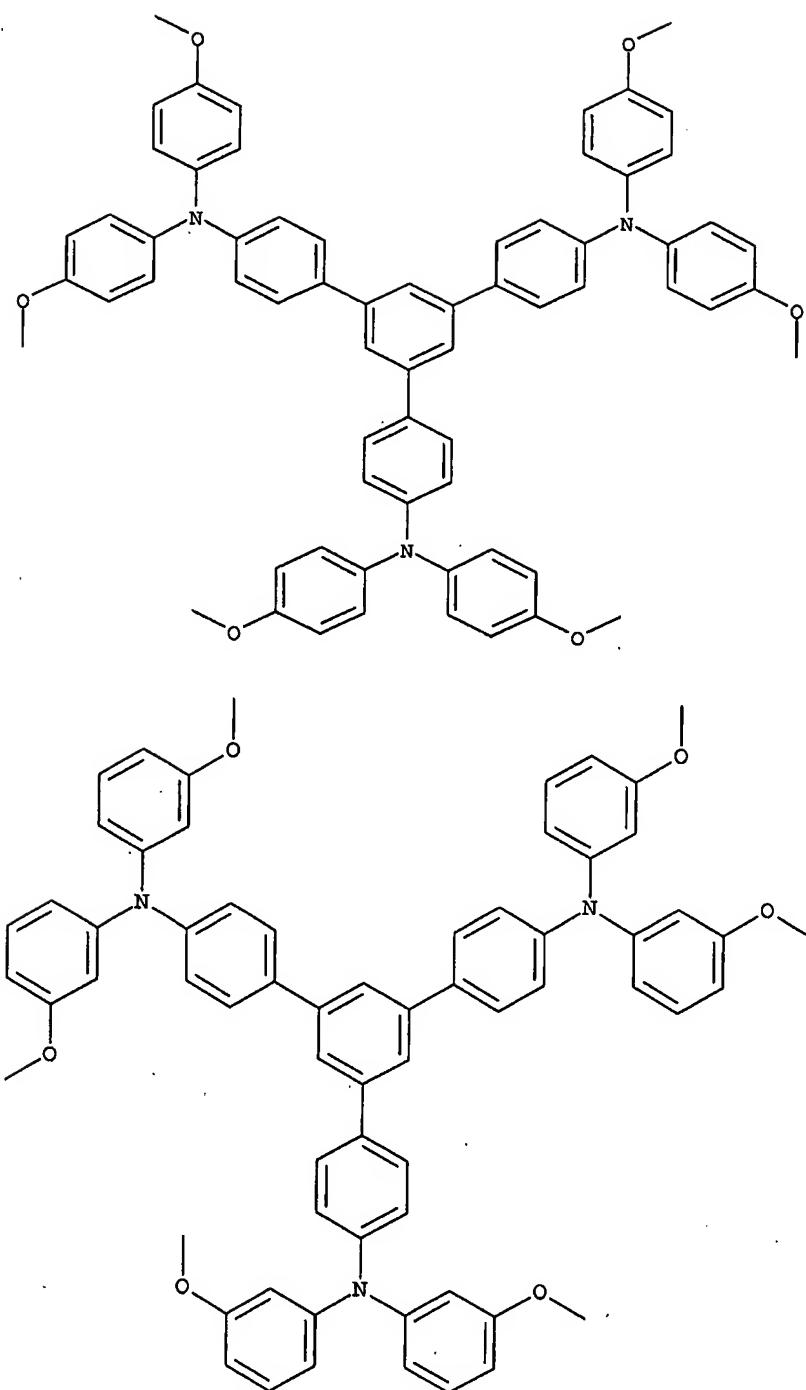
15

9. Photovoltaic device according to claim 8, wherein said 1,3,5-tris-aminophenyl-benzene compound represented by formula (I) is selected from the group consisting of:

AMENDED SHEET (ARTICLE 19)

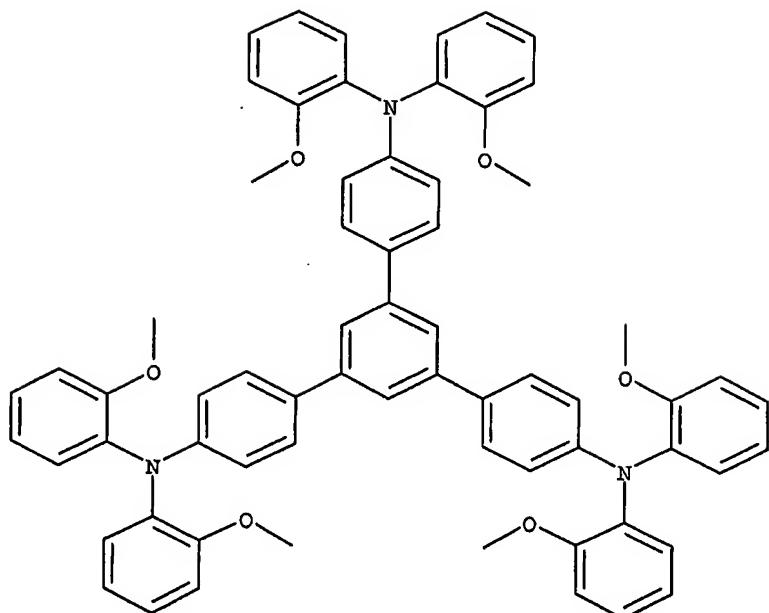


AMENDED SHEET (ARTICLE 19)



5 and

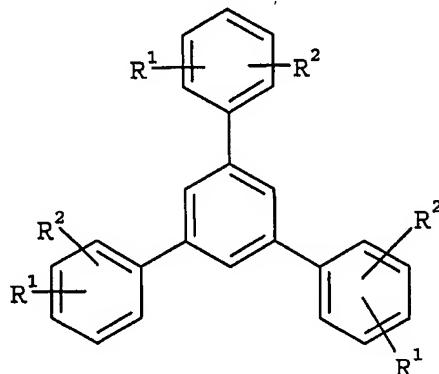
AMENDED SHEET (ARTICLE 19)



10. Photovoltaic device according to claim 8, wherein said n-type semiconductor is selected from the group consisting of titanium oxides, tin oxides, niobium oxides, tantalum oxides, tungsten oxides and zinc oxides.
11. Photovoltaic device according to claim 8, wherein said photovoltaic device further contains at least one spectral sensitizer.
12. Photovoltaic device according to claim 8, wherein said photovoltaic device further contains at least one spectral sensitizer selected from the group consisting of metal chalcogenide nano-particles with a band-gap of less than 2.9 eV, organic dyes and metallo-organic dyes.
13. Photovoltaic device according to claim 8, wherein said photovoltaic device further contains at least one spectral sensitizer selected from the group consisting metal oxides, metal sulphides and metal selenides.

AMENDED SHEET (ARTICLE 19)

14. A process for preparing a photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):



5       wherein R<sup>1</sup> represents a -NR<sup>3</sup>R<sup>4</sup> group, wherein R<sup>3</sup> and R<sup>4</sup>, same or  
 10      different, represents a C<sub>2</sub>-C<sub>10</sub> alkyl group including said alkyl  
       groups in substituted form, a benzyl group, a cycloalkyl group,  
       or an aryl group, and R<sup>2</sup> represents hydrogen, an alkyl group  
 15      including a substituted alkyl group or halogen, with at least one  
       transparent electrode comprising the steps of: providing a  
       support with a conductive layer as one electrode; coating said  
       conductive layer on the support with a layer comprising said n-type  
       semiconductor with a bandgap of greater than 2.9 eV; coating  
 20      said n-type semiconductor-containing layer with a solution or  
       dispersion comprising said 1,3,5-tris-aminophenyl-benzene  
       compound, or cation thereof, to provide after drying a layer  
       comprising said 1,3,5-tris-aminophenyl-benzene compound; and  
       applying a conductive layer to said layer comprising said 1,3,5-  
       tris-aminophenyl-benzene compound thereby providing a second  
       electrode.

AMENDED SHEET (ARTICLE 19)

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/10120A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 H01L51/20 H01L51/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 197 11 713 A (HOECHST AG) 1 October 1998 (1998-10-01) the whole document ---	1-4, 7
Y	US 5 487 953 A (SHIROTA YASUHIRO ET AL) 30 January 1996 (1996-01-30) the whole document ---	1-4, 7
Y	HAGEN ET AL: "Novel hybrid solar cells consisting of inorganic nanoparticles and an organic hole transport material" SYNTHETIC METALS, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 89, September 1997 (1997-09), pages 215-220, XP002108277 ISSN: 0379-6779 the whole document ---	1, 3, 4, 7

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the International filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

- \*&\* document member of the same patent family

Date of the actual completion of the International search

Date of mailing of the International search report

14 May 2003

21/05/2003

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Königstein, C

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/10120

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Category	Relevant to claim No.
Y	ITANO K ET AL: "FABRICATION AND PERFORMANCES OF A DOUBLE-LAYER ORGANIC ELECTROLUMINESCENT DEVICE USING A NOVEL STARBUST MOLECULE, 1,3,5-TRISUN-(4-DIPHENYLAMINOPHENYL)PHENYL AMINOBENZENE, AS A HOLE-TRANSPORT MATERIAL AND TRIS(8-QUINOLINOLATO)ALUMINUM AS AN EMITTING MATERIAL" IEEE TRANSACTIONS ON ELECTRON DEVICES, IEEE INC. NEW YORK, US, vol. 44, no. 8, 1 August 1997 (1997-08-01), pages 1218-1221, XP000658323 ISSN: 0018-9383 the whole document ----	1,3,4,7
A	EP 1 176 646 A (ECOLE POLYTECH) 30 January 2002 (2002-01-30) the whole document ----	1,5,6
A	EP 0 901 175 A (FUJI PHOTO FILM CO LTD) 10 March 1999 (1999-03-10) the whole document ----	
A	EP 0 349 034 A (AGFA GEVAERT NV) 3 January 1990 (1990-01-03) cited in the application the whole document ----	

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/EP 02/10120

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
DE 19711713	A	01-10-1998	DE 19711713 A1 WO 9848433 A1 EP 0968507 A1 JP 2001525108 T US 6335480 B1	01-10-1998 29-10-1998 05-01-2000 04-12-2001 01-01-2002
US 5487953	A	30-01-1996	JP 7090256 A	04-04-1995
EP 1176646	A	30-01-2002	EP 1176646 A1 AU 5771101 A JP 2002111031 A US 2002017656 A1	30-01-2002 31-01-2002 12-04-2002 14-02-2002
EP 0901175	A	10-03-1999	JP 11144773 A AT 222028 T DE 69807015 D1 DE 69807015 T2 EP 0901175 A2 US 6084176 A	28-05-1999 15-08-2002 12-09-2002 17-04-2003 10-03-1999 04-07-2000
EP 0349034	A	03-01-1990	DE 68912216 D1 DE 68912216 T2 EP 0349034 A1 JP 2118666 A US 4923774 A	24-02-1994 28-07-1994 03-01-1990 02-05-1990 08-05-1990